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Extended interface layer concept for higher stability and improvement of life time in bulk heterojunction solar cells

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Power conversion efficiency (PCE) of bulk heterojunction (BHJ) organic solar cells has reached above ~10%. These BHJ cells have potential for flexible thin films at low processing temperatures using roll to roll printing on flexible substrates. Further, the basic materials properties can be tailored through organic synthetic routes. However, the issues related to its durability should be addressed before its commercialization. Hence, a conventional solar cell of the poly (3-hexylthiophene) (P3HT) :(6, 6)-phenyl-C_{61}butyric acid methyl ester ($PC_{61}BM$) blend on ITO substrates was fabricated, and investigated, which shows improved life time by using a combinational Ca/Al cathode, wherein the deposition of calcium layer is extended beyond the aluminum layer. The extended deposition of calcium layer beyond aluminum prevents the edge degradation by its oxidation and hence protecting the active pixel area of the device, resulting in the improvement of life time of device from ~80 hours to ~ 400 hrs. [http://dx.doi.org/10.1063/1.4907986]

Polymer photovoltaic has already established its immense promise as a futuristic, cost effective and large area efficient solar cell technology.[1–3] The power conversion efficiency (PCE) between 8-11%[4] has already been achieved in single junction as well as in tandem solar cell based on conventional and inverted device configurations. However, in spite of these high efficiencies there is serious bottleneck in the commercialization of organic solar cells which is their stability[5] i.e., degradation in the efficiency with time. The primary reason for the less life time is the degradation of the donor-acceptor active layer with the attack of ambient condition, in particularly by H_2O[6] and O_2 from the nanopore of the top cathode electrode. As such the encapsulation with using glass and epoxy[7–9] (along with LiF prior to Al to cathode is being used) is globally utilized for the life time improvement. The device thus encapsulated shows life time improvement[10,11] than the unencapsulated one. However, it is still not adequate for the commercial vibrant.[1] In fact it is globally realized that ~10% efficiency and life time more than 5000 hours may enable the commercialization of polymer solar cells. In view of this technological need there is a global R& D thrust to address the stability of PCE by improving the life time by its innovative means.[12–14] The present paper addresses the life time improvement issue which incorporates the innovation of depositing the extended calcium (Ca) layer (more than the dimension of aluminum layer) which enables the oxidation of extended portion of calcium cathode. The calcium oxide so formed due to ambient exposure in turn protects the attack from the ambient condition drastically from a few hours to a few hundred hours, to be precise the improvement in life time of P3HT:$PC_{61}BM$ based organic solar cells from ~ 80 hours to

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~ 400 hours from an unextended calcium interface layer to extended one. This concept of extended cathode oxide layer for improving the life time of device has been demonstrated in a simplest device configuration ITO/MoO_3(10nm)/P3HT:$PC_{61}BM$ (~90nm)/Ca(~15nm)/Al(100nm) which gives PCE ~ 2% and life time of the order of ~ 400 hours. The paper is being sent for communication as an advanced idea and for R& D of higher efficiency devices with this new extended calcium layer idea is in progress. In fact a patent filing[15] is in process.

P3HT was purchased from 1-material. $PC_{61}BM$, o-dichlorobenzene, 1,8-diiodooctane, Calcium and Aluminum were sourced from Aldrich. The materials were used as received without any further purification. Patterned ITOs were cleaned ultrasonically in deionized water, hot trichloroethylene, acetone and isopropanol. The ITO was UV-ozone treated for 10 minutes. Devices were fabricated in glove box under Nitrogen pressure. MoO_3(10 nm) was thermally evaporated in vacuum chamber. The P3HT:$PC_{61}BM$ blend in the ratio of 1:0.6, in a dichlorobenzene solution (30 mg/mL) was spin coated at 900 rpm to give thickness of about ~ 90nm. Calcium and Al was thermally evaporated using shadow mask. The active area of the device was 0.06 cm^2. The samples were taken out for photovoltaic test in air at ambient conditions at ~25^0C. Current - Voltage (I-*V*) characteristic were measured using a Keithley 2420 under 100 mW/cm^2 simulated AM 1.5 G solar illumination. The light intensity was measured using a calibrated Si photo detector.

Figure 1(a) and 1(b) show the oxygen attack of top electrode (Calcium/Aluminum). Oxygen attacks the top surface as well as the edges of the metal electrode. One strategy to protect the top surface is by increasing the thickness of the top electrode. By doing this, the device lifetime increases significantly because oxygen now cannot penetrate through the top surface. But the edges are still exposed and continue to degrade. The oxidation from the edges will reduce the pixel area and also influences the electrode-organic interface. The situation becomes even worse when one wants to use reactive metals like calcium.[16,17] Capping by aluminum or increasing the thickness of the top electrode does not prevent the oxidation of edges. To the best of our knowledge there is no simple strategy proposed to address the degradation of edges other than encapsulation. Herein, we present a simple strategy to arrest the degradation of edges. Since oxide layer inhibits oxygen permeation then it makes sense to extend the top contact metal layer beyond the pixel boundaries in horizontal direction as well. Oxygen will attack on the extended part of the metal and thus the formed oxide layer will reduce further oxygen permeation through the edges. To confirm this hypothesis, we chosen P3HT and $PC_{61}BM$ as the materials of choice for the active layer. This choice is judicious because P3HT is less susceptible to photo-degradation than other polymers. This particular blend has been shown to have greater stability,[18] to have a stable bottom contact we used MoO_3 which is also resistive to atmospheric condition. The layer of interest in this study is calcium which reacts very fast and degrades within few seconds. This layer is evaporated beyond the pixel boundaries using an extended shadow mask. The top surface of the calcium is protected by evaporating aluminum using a regular shadow mask to define the pixel area. Figure 1 shows the schematic of devices fabricated using a regular and an extended mask. Two types of devices were fabricated.

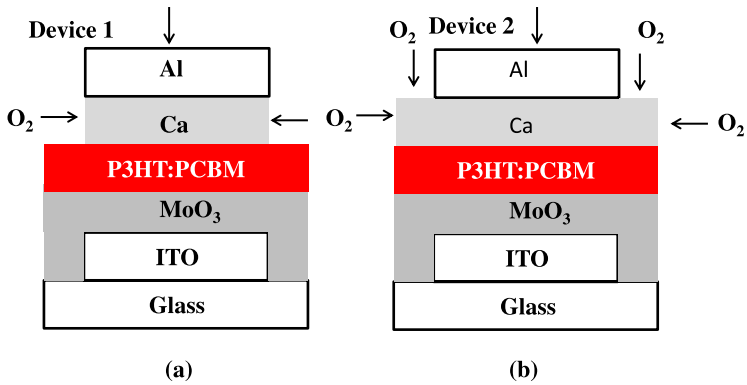

FIG. 1. Schematic of the device fabricated (a) using regular mask for calcium and Aluminum evaporation (Device 1) (b) an extended mask for calcium evaporation (Device 2).

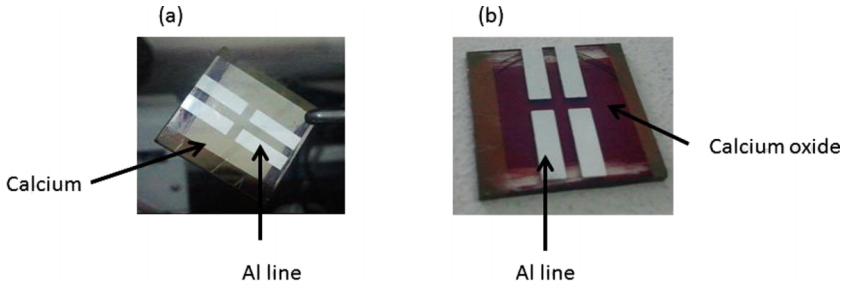

FIG. 2. Shows the P3HT:$PC_{61}BM$ based fabricated devices, with extended Ca cathode inside the glove box (a) and extended Ca calcium cathode when taken in ambiance (b).

For the sake of convenience devices are named as device 1 and device 2 respectively. In device 1 (Figure 1(a)) calcium and aluminum are evaporated using the same shadow mask whereas in device 2 (Figure 1(b)) calcium is evaporated beyond the pixel boundaries using an extended shadow mask. It is important to mention here that the uncapped calcium in device 2 losses its metallic shine within few seconds of its exposure to oxygen (Figure 2). As such it forms a translucent calcium oxide film which inhibits oxygen and moisture attack to the device.

Figure 3(a) and 3(b) show the J-V characteristics of the devices 1 and 2, respectively under AM 1.5G illumination. The PCE of these simple structure fresh (just after preparation) devices 1 and 2 when measured in air was approximately 2.0 %. It is interesting to note that both the devices

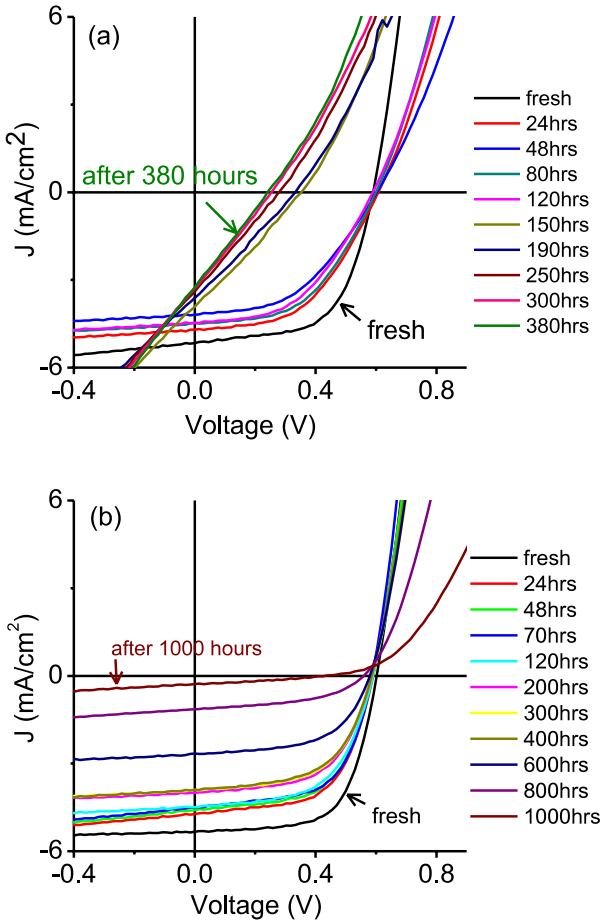

FIG. 3. J-V characteristic of devices 1 in (a) and device 2 in (b) under AM 1.5 G illuminations after different time intervals.

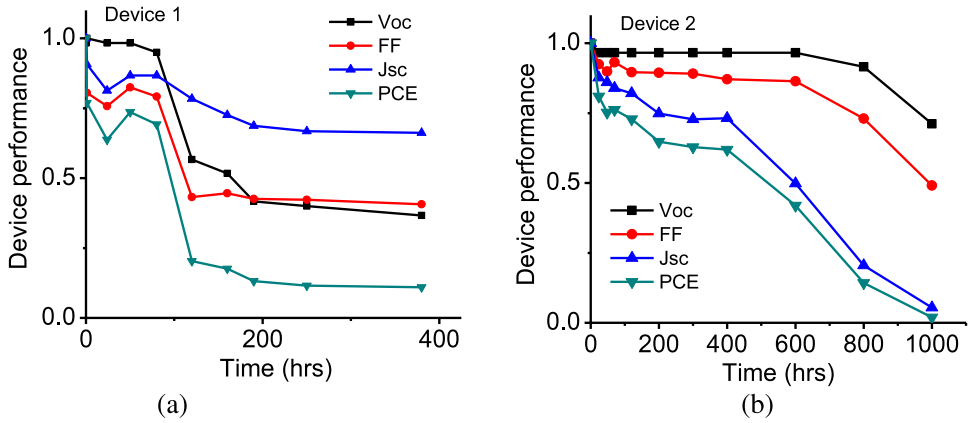

FIG. 4. Performance of device 1 and device 2 in terms of normalized J_{sc}, V_{oc}, PCE and FF in 4(a) and 4(b) respectively.

have high fill factor of greater than 60% in the beginning suggesting that the charge extraction is efficient. When the degradation of the two devices was studied as a function of time it has been found that the device 1 degrades faster in comparison to device 2. Further, it is abundantly clear from the J-V curves in Figure 3(a) and 3(b) that in device 1 the leakage current becomes high and V_{oc} reduces significantly with time. The explicit variation of normalized parameters such as V_{oc}, J_{sc}, FF and PCE of all devices with time are shown in Figure 4. The V_{oc} of both the fresh devices 1 and 2 is 0.59 V. The V_{oc} of the device 1 starts decreasing quite steadily upto ~ 80 hours as can be seen in Figure 4(a) and then it drops significantly to 0.34V after 120 hours. Further, this device starts giving large leakage current and its V_{oc} drops to 0.2V after 380 hours (Figure 4(a), 3(a)). This decrease in the V_{oc} of device 1 has been attributed to contact degradation through the edges. In contrast to this the V_{oc} in case of device 2 remains constant over a period of 600 hours as shown in Figure 4(b). However, beyond 600 hours the V_{oc} in device 2 starts decreasing at a faster rate but still less as compared to the device 1. This enhanced stability in V_{oc} in case of device 2 has been attributed to the reduced edge degradation owing to the formation of protecting calcium oxide layer in the horizontal direction. Further J_{sc} of devices 1 and 2 decreases slowly in a very similar fashion. Here it is very important to mention that we have fabricated five devices in two independent runs and average life time of device 2 architecture is ~ 400±60 hours and that of the device 1 is ~80±30 hours. The life time of these devices vary with the humidity, temperature as well as with the light exposure time.[10] However, it is not of our interest in present investigation. For the clarity point of view we want to elaborate that normally when measuring the degradation of a device, J_{sc}, FF and PCE show a continuous and steady percentage decrease with time. The change in V_{oc} of the device is normally slow and it remains more than 80% of its initial value for a longer period. But in the case of the breakdown of the device (like shunt, large leakage current etc) the V_{oc} changes abruptly (such as in Figure 4(a) for device 1). It is frequently encountered that devices breakdown even before reaching the half of the initial PCE. In such a case it makes sense to define a breakdown time. It may be defined as the time when the device losses its V_{oc} by 30%. As can be seen from Figure 3(a) or 4(a), In device 1 the breakdown occurs even before reaching the half PCE. The average breakdown time in the device 1 architecture was measured to be 80 ±30 hours. However, V_{oc} of the fresh device 2 was 0.59V and it changes slowly. After ~800 hours in ambient room temperature conditions it drops to 0.55V which is about 93% of its initial value. The breakdown time in device 2 is 1000 ± 150 hours because the V_{oc} at this time is 0.43V which is about 70% of its initial value 0.59V.

The FF of the fresh device2 was 66% and after 800 hours it drops to 49%. The device parameters J_{sc} and PCE have shown relatively faster decay (Figure 4(b)). The J_{sc} and PCE of the fresh device 2 was 5.3(mA/cm^2) and ~2.1 respectively. After 800 hours J_{sc} drops to 1.14 (mA/cm^2) and PCE drops to 0.31%. The average half lifetime of the device 2 is measured to 400 ± 60hours. The device 2 when measured after 1000 hours was found to be degraded. It can also be seen from the J-V in the above Figure 3(a) and 3(b) that there is continuous increase in the series resistance with time.

The increase in series resistance with time is likely due to degradation of cathode contact (Ca/Al) since the anode contact is made using MoO_3 which is air stable. Hence in view of these observations we can say that the device 2 certainly outperforms device 1 in terms of longevity which is primarily due to stabilized V_{oc}, low series resistance and high shunt resistance. The increased lifetime of device 2 than device 1 is attributed to decrease in the edges oxidation.

In summary, we have demonstrated that the degradation of edges of electrodes based on reactive metals can be reduced by extending its deposition in the lateral direction. Reactive metal forms an oxide layer at the edges which inhibits oxygen permeation and protects the active pixel area hence enhancing its life time. The current investigation highlights the importance of edges degradation especially in the case of reactive cathodes.

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[1] F.C. Krebs, N. Espinosa, M. Hösel, R. R. Søndergaard, and M. Jørgensen, Adv. Mater **26**, 29 (2014).
[2] J. Nelson, Mater. Today **14**, 462 (2011).
[3] G. Li, R. Zhu, and Y. Yang, Nat. Photonics **6**, 153 (2012).
[4] M. A. Green, K. Emery, Y. Hoshikawa, W. Warta, and E.D. Dunlop, Prog. Photovoltaics **22**, 1 (2014).
[5] M. Jørgensen, K. Norrman, S. A. Gevorgyan, T. Tromholt, B. Andreasen, and F.C. Krebs, Adv. Mater **24**, 580 (2012).
[6] K. Norrman, S. A. Gevorgyan, and F.C. Krebs, ACS Appl. Mater Interfaces **1**, 102 (2009).
[7] A. Asadpoordarvish, A. Sandström, S. Tang, J. Granström, and L. Edman, Appl. Phys. Lett. **100**, 193508-1 (2012).
[8] H. Cao, W. He, Y. Mao, X. Lin, K. Ishikawa, J. H. Dickerson, and W.P. Hess, J. Power Sources **264**, 168 (2014).
[9] S. K. Ramdas, S. J. Chua, and L.K. Ke, Patent **2011**, US 20110132449 A1.
[10] C. H. Peters, I.T. Sachs-Quintana, J.P. Kastrop, S. Beaupre, M. Leclerc, and M.D. McGehee, Adv. Energy Mater. **1**, 491 (2011).
[11] C. Lungenschmied, G. Dennler, H. Neugebaueeer, S. N. Sacrifiti, M. Glatthaar, T. Meyer, and A. Meyer, Sol. Energy Mater. Sol. Cells **91**, 379 (2007).
[12] W. R. Matker, J. D. Dauglas, C. Cabanetos, I. T. Sachsquintana, J. A. Bartelt, E.T. Hoke, A. E. Labban, P.M. Beaujuge, J. M. J. Frechet, and M. D. McGehee, Energy Environ. Sci. **6**, 2529 (2013).
[13] W. Yang, Y. Yao, and C. Q. Wu, Org. Electron. **14**, 1992 (2013).
[14] J.Y. Oh, M. Shin, H.W. Lee, Y. J. Lee, H. K. Baik, and U. Jeong, ACS Appl. Mater Interfaces **6**, 7759 (2014).
[15] F. Ali, A. Sharma, J.P. Tiwari, and S. Chand, Provisional Indian Patent 00943DEL2014.
[16] B. Paci, A. Generosi, V. R. Albertini, P. Perfetti, R. D. Bettignies, and C Sentein, Chem. Phys. Letters **461**, 77 (2008).
[17] M. O. Reese, M. S. White, G. Rubles, D.S. Ginley, and S. E. Shaheen, Appl. Phys. Lett. **92**, 053307-1 (2008).
[18] M. H. Kwon, Trans. on electrical. and electronic mater. **13**, 98 (2012).